A comparative study of some newly synthesized ligands with some alkaloid containing plants as corrosion combating agents on some metals in acid media.

नवीन संश्लेषित लिगेण्डों का क्षाराभ युक्त पादपों के साथ अम्लीय माध्यम में संक्षारण प्रतिरोधकों के रूप में तुलनात्मक अध्ययन ।

A

SYNOPSIS

Submitted for the Award of Ph.D. degree of

Maharshi Dayanand Saraswati University, Ajmer

In the faculty of Science (Chemistry)

By

Anuja Khed

Under Supervision of

Dr. R. K. Upadhyay

Lecturer (Selection Scale)

Department Of Chemistry

Samrat Prithviraj Chouhan Government College, Ajmer

APPENDIX – IV

Format for Outline of Proposed Research Work

(To be supplied in Eight copies)

1. Name of Scholar(In English) :- **Anuja Khed**

   (In Hindi) :- अनुजा खेड

2. Title of Research Work :- **A comparative study of some newly synthesized ligands with some alkaloid containing plants as corrosion combating agents on some metals in acid media.**

   (In English)

   (In Hindi) :- नवीन संश्लेषित लिगेण्डों का क्षाराभ युक्त पादपों के साथ अम्लीय माध्यम में संक्षारण प्रतिरोधकों के रूप में तुलनात्मक अध्ययन ।

3.Location

(a) Institution/Department where the work is to be done — Department of chemistry , Samrat Prithviraj Chouhan Government College,Ajmer.

(b)Geographical area of investigation, If any : — NIL

4.Importance of proposed investigation — **Annexure – I**

5. Review of work already done on the subject of proposed Research Study — **Annexure – II**

6. Research Gaps identified in the proposed field of investigation. — **Annexure – III**

7. Major Hypothesis, If any — **Annexure – IV**

8. Research Methodology. — **Annexure – V**

9. List of References cited — **Annexure – VI**

Signature of candidate with date

Outline Aproved.

Name and Signature of supervisor with date and seal.

Annexure I

Importance of proposed investigation

Corrosion is a destructive phenomenon which is chemical or electrochemical in nature[1,2]. Corrosion not only changes the physical and chemical properties of metals and alloys but it also decreases strength and other features also which restricts the metal from its specific uses. The results of corrosion effects the efficiency and lasting of a metal which results in the change of machinery, parts, container of a particular metal after certain interval of time.

This affects not only the manufacturing process but also the cost of production. There is a large loss of economy due to corrosion of materials in industries. Corrosion is a very serious problem being faced by various industries all across the world. The problem is more prominent for the industries which have their basic machinery and tools being made up of metals like aluminium , mild steel, lead, tin copper *etc*. These industries spend a lot of their funds to fight against corrosion which if ,not taken seriously , hinder their production , make their equipments and tools under-efficient as well as can be a major cause of decay of key parts of important heavy machineries used in the construction of buildings, bridges, railway tracks *etc* . Thus it is very important to investigate certain synthesized compounds as well as certain naturally occurring plants as corrosion combating agents. The environmental toxicity of organic corrosion inhibitors has prompted the search for green corrosion inhibitors as they are biodegradable, do not contain heavy metals or other toxic compounds. As in addition to being environmentally friendly and ecologically acceptable, plant products are inexpensive, readily available and renewable. Investigations of corrosion inhibiting abilities of tannins, alkaloids, organic amino acids, and organic dyes of plant origin are of interest.

Many organic compounds having hetero atoms like O, N, S etc have been studied as corrosion combating agents[3-5] for metals like Aluminium, Iron, Copper, Zinc, Tin etc[6] which are generally used in industries. Also some naturally occurring products like Opuntia,[7] Gulmohar,[8] Neem,[9] Trifla,[10] Saunf[11] *etc* have also been studied as corrosion inhibitors. The present study has its importance that some new ligands will be synthesized in the laboratory and some naturally occurring plants found in the nearby areas will be studied as corrosion combating agents. Simultaneously they will be studied for the same metal in same acidic media in same environmental conditions to know a comparative effectiveness of two combating agents.The importance of present study lies in the observation that two categories of corrosion combating agents are equally effective or have advantages over each other costwise, effectiveness and ecologically.

Annexure II

Review of work already done on the subject of proposed Research Study

In recent years, sol-gel coatings doped with inhibitors show real promise.[12] Although substantial research has been devoted to corrosion inhibition by plant extracts, reports on the detailed mechanisms of the adsorption process and identification of the active ingredient are still scarce. Development of computational modeling backed by wet experimental results would help to fill this void and help understand the mechanism of inhibitor action, their adsorption patterns, the inhibitor-metal surface interface and aid the development of designer inhibitors with an understanding of the time required for the release of self-healing inhibitors.

Over the years, considerable efforts have been deployed to find suitable corrosion inhibitors of organic origin in various corrosive media.[13-16] In acid media, nitrogen-base materials and their derivatives, sulphur-containing compounds,[17,18] aldehydes, thioaldehydes, acetylenic compounds, and various alkaloids, for example, papaverine, strychnine, quinine, and nicotine are used as inhibitors. In neutral media, benzoate, nitrite, chromate, and phosphate act as good inhibitors. Inhibitors decrease or prevent the reaction of the metal with the media. They reduce the corrosion rate by

(i)adsorption of ions/molecules onto metal surface,

(ii)increasing or decreasing the anodic and/or cathodic reaction,

(iii)decreasing the diffusion rate for reactants to the surface of the metal,

(iv)decreasing the electrical resistance of the metal surface.

(v)inhibitors that are often easy to apply and have in situ application advantage.

Pyridine and derivatives are believed to exhibit good protection against corrosion in acidic media.[19] These inhibitors have also found useful application in the formulation of primers and anticorrosive coatings, but a major disadvantage is their toxicity and as such their use has come under severe criticism. Among the alternative corrosion inhibitors, organic substances containing polar functions with nitrogen, sulphur, and/or oxygen in the conjugated system have been reported to exhibit good inhibiting properties.[20-23]

In addition to above studies some workers have also tried certain natural products like Pomegranate,[24] Gooseberry,[25] Shikakai,[26] Banana,[27] Khejri[28] *etc* as corrosion combating agents.

Since many of these contain heteroatom like N, O, S *etc* in their extract of leaf, stem, root, seed, fruit *etc*, so they may also be found as good corrosion inhibitors.

E. E. Ebenso used papaya leaves as corrosion inhibitor for mild steel in acidic media.[29]

A. Y. El-Etre used natural honey as corrosion inhibitor for copper in aqueous media.[30]

Essential oils of rosemary have been used as corrosion inhibitor for metals.[31]

Extracts of *Raphia hookeri*,[32] guar gum,[33] *Allium sativum*,[34] *Carica papaya*,[35] *Garcinia kola*,[36] *Phyllanthus amarus*,[37] jojoba oil,[38] Artemisia oil,[39] *Occimum viridis*,[40] *Argemone Mexicana*,[41] *Ocimum sanctum* (Holy Basil)[42] have also been studied as corrosion combating agent.

Some Schiff's Bases have also been studied earlier as corrosion inhibitors for mild steel and aluminium in acid media of different concentrations.[43-45]

Annexure III

Research Gaps identified in the proposed field of investigation

Inhibitors are often added in industrial processes to secure metal dissolution from acid solutions. Standard anti corrosion coatings developed till date passively prevent the interaction of corrosion species and the metal. The known hazardous effects of most synthetic organic inhibitors and the need to develop cheap, nontoxic and eco-friendly processes have now urged researchers to focus on the use of natural products. Increasingly, there is a need to develop sophisticated new generation coatings for improved performance, especially in view of Cr VI being banned and labeled as a carcinogen.[46] The use of inhibitors is one of the best options of protecting metals against corrosion. Several inhibitors in use are either synthesized from cheap raw material or chosen from compounds having hetero atoms in their aromatic or long-chain carbon system. However, most of these inhibitors are toxic to the environment. This has prompted the search for green corrosion inhibitors.

Although a number of synthesized ligands have been studied as corrosion inhibitors for metals and alloys in acidic media.[47-49] Most of these ligands have been synthesized from organic compounds which are costly, toxic and environment polluting. On the other hand, many natural products have also been studied as corrosion combating agents for certain metals and alloys.[50-52] But these two studies have been carried out separately by separate workers. No serious attempts have been made to use synthesized ligands and naturally occurring plants as corrosion inhibitors in same corrosive conditions for same metals in the same acidic media. It will be interesting to monitor the inhibitive effects of these two agents in same conditions.

Annexure IV

Major Hypothesis

Hereby, it is a well known fact that ligands obtained from alkaloid containing plants like *Murraya koenigii* (Meetha Neem)and *Catharanthus roseus* (Sadabahar) contain nitrogen and other hetero atoms . Therefore, they will also prove to be effective corrosion inhibitors as hetero atom containing compounds have been established as effective corrosion inhibitors in various previous studies.

Efforts to find natural organic substances or biodegradable organic materials to be used as corrosion inhibitors over the years have been intensified. Several reports are available on the various natural products used as green inhibitors. Low-grade gram flour, natural honey, onion, potato, gelatin, plant roots, leaves, seeds, and flowers gums have been reported as good inhibitors. However, most of them have been tested on steel and nickel sheets. Although some studies have been performed on aluminum sheets, the corrosion effect is seen in very mild acidic or basic solutions (millimolar solutions).

Success of investigation will reduce dependence on various type of traditional inhibitors in the industrial field as well as open new horizons in the discovery of natural inhibitors towards fighting against the most disastrous problem being faced by the industries since time immemorial i.e. corrosion.

Natural inhibitors synthesized from plant extracts would focus on 3Es *viz* ECONOMIC , EFFECTIVE and far more ECO-FRIENDLY .

Main focus of the present study will be to observe the corrosion combating efficiency of some newly synthesized ligands and some naturally occurring plants which are very economic, easily available, environment friendly and non toxic.

The main hypothesis of present work is to compare these studies and to find out whether naturally occurring plants are simply economic or they are more effective than synthesized ligands. The success of present study lies in the fact that an inhibitor must not only be economic and eco-friendly but also should be highly effective because effectiveness cannot be ignored at the cost of economy.

Annexure – V

Research Methodology

Materials required to synthesize some ligands are aldehydes, ketones, primary amines, secondary amines and extract of some plants containing alkaloids.

Method :-

Structural determination techniques like FT-IR / NMR would be used for the characterization of proposed ligands synthesized in laboratory.

Following are the four methods that would be employed for measuring corrosion rate, inhibition efficiency and coverage of the metallic surface.

1. **Weight Loss Method :-**
   In this method the specimen is weighed before and after the exposure in corrosive media, to determine the amount of metal lost . Weight is taken after removing all the adherent corrosion products. Thus inhibition efficiency (η%) can be calculated from the above data as[53] :-

$$\boldsymbol{\eta\ \% = \frac{\Delta Wu - \Delta Wi}{\Delta Wu} \times 100}$$

Where ,

W_u is the weight loss in uninhibited solution and

W_i is the weight loss in inhibited solution

Corrosion rate in $\left(\frac{mm}{yr}\right)$ can be calculated by following equation[54] –

$$\textbf{Corrosion Rate } \left(\frac{\textbf{mm}}{\textbf{yr}}\right) = \frac{\textbf{87.6 } \Delta \textbf{W}}{\textbf{DAT}}$$

Where, ΔW is weight loss in mg, D is the metal density in $g.cm^{-3}$, A is the exposed area in cm^2 , T is the time of exposure in hours .

2. **Thermometric Method :-**
   In thermometric method , the temperature variation of the solution is plotted as a function of time . The specimen and the thermometer are immersed in the solution for test. The temperature of the system remain almost constant initially then increases and attain a maximum value and then starts to decrease. According to Mylius inhibition efficiency (η%) can be calculated as[55] :-

$$\eta\% = \frac{(\mathbf{RNu} - \mathbf{RNi})}{\mathbf{RNu}} \times \mathbf{100}$$

Where ,

RN_u is the reaction number in uninhibited solution,

RN_i is the reaction number in inhibited solution

Reaction Number (RN) can be calculated in terms of temperature as[56] –

$$\mathbf{Reaction\ Number} = \frac{(\mathbf{Tm} - \mathbf{Ti})}{\mathbf{t}}$$

where,

T_m is the maximum temperature of the test solution,

Ti is the initial temperature of the test solution and

t is the time in minutes to attain maximum temperature

3. **Potentiostatic Method :-**
   Potentiostatic method is a polarization technique that allows for the controlled polarization of metal surface in electrolyte in order to observe cathodic and anodic behaviors . Corrosion reactions will be monitored on a sample of desired metal . A number of characteristics of the metal/environment pairing will be determines through this technique[57].

Polarization experiments are performed with a computer controlled potentiostat. The metal sample is known as working electrode (WE) , which can be either bare metal or coated. The reference electrode (RE) should typically be a material that is very stable under the test conditions . The RE will be used to monitor and maintain potential at the WE surface. A potentiostat monitors ionic current passing through the electrolyte between the counter electrode(CE) and the WE , and electron current passing between the CE and WE.

4. **Scanning Electron Microscope Method :-** Surfce examination of sample can be done by using Scanning Electron Microscope (SEM) technique that includes magnification upto 30000 times with corresponding resolution enhancement and 5 kv and 15 kv operation.
   SEM for the sample in pure state, dipped in acid solution and also in acid solution with inhibitor will be carried out. The SEM studies of the sample will show the surface structural changes in the sample[58].

Annexure – VI

List of References cited

1. Anonymous, Bull. Amer, Zinc inst., **11**,82, 1928.
2. W.R. Whitney, *J. Amer, Chem. Soc.***25**,394,1903.
3. V. B. Singh and S.M.A. Hosseini , *J. App. Electrochem.* **24**, 250, 1994.
4. R. S. Dubey , *Bull. Electrochem.* **12,** 467, 1996.
5. S. I. Sato and N. masuko , *J. Electrochem. Soc.* **138,** 3705, 1995.
6. H.Avner..,Introduction of physical metallurgy and process metallurgy 2000.
7. A. Y. El-Etre, *" Inhibition of aluminium corrosion using Opuntia extract," Corrosion Science,* vol.45, no. 11, **2485-2495,** 2003.
8. O. K. Abiola, N. C. Oforka, E. E. Ebenso, and N. M. Nwinuka, *"Eco-friendly corrosion inhibitors: The inhibitive action of Delonix Regia extract for the corrosion of aluminium in acidic media," Anti-Corrosion Methods and Materials,* vol. 54, no. 4, **219–224,** 2007.
9. U. J. Ekpe, E. E. Ebenso, and U. J. Ibok, *"Inhibitory action of Azadirachta indica leaves extract on the corrosion of mild steel in H_2SO_4," West African Journal of Biological and Applied Chemistry,* vol. 37,**13–30**, 1994.
10. M. J. Shangvi, S. K. Shukla, A. N. Mishra, M. R. padh, and G. N. Mehta, *"Corrosion inhibition of mild steel in hydrochloric acid by acid extracts of Sapindus Trifolianus, Acacia Concian and Trifla,"Transactions of the Metal Finishers Association of India,* vol. 5, no. 3,**143–147**, 1996.
11. N. Lahhit, A. Bouyanzer, J.-M. Desjobert, et al., *"Fennel (Foeniculum vulgare) essential oil as green corrosion Inhibitor of carbon steel in hydrochloric acid solution," Portugaliae Electrochimica Acta,* vol. 29, no. 2,**127–138**, 2011.
12. A. Pepe, M. Aparicio, S. Ceré, and A. Durán, *"Preparation and characterization of cerium doped silica sol-gel coatings on glass and aluminum substrates," Journal of Non-Crystalline Solids,* vol. 348, **162–171**, 2004.
13. M. Bouklah, B. Hammouti, T. Benhadda, and M. Benkadour, *"Thiophene derivatives as effective inhibitors for the corrosion of steel in 0.5 M H_2SO_4," Journal of Applied Electrochemistry,* vol. 35, no. 11,**1095–1101**, 2005.
14. A. S. Fouda, A. A. Al-Sarawy, and E. E. El-Katori, "*Pyrazolone derivatives as corrosion inhibitors for C-steel HCl solution," Desalination,* vol. 201,**1–13**, 2006.
15. A. Fiala, A. Chibani, A. Darchen, A. Boulkamh, and K. Djebbar, *"Investigations of the inhibition of copper corrosion in nitric acid solutions by ketene dithioacetal derivatives," Applied Surface Science,* vol. 253, no. 24, **9347–9356**, 2007.
16. U. R. Evans, *The Corrosion and Oxidation of Metals,* Hodder Arnold, 1976.
17. W. Y. Wing and W.T Wong, *J. Organometallic., Chem.*, **48**, 584, 1999
18. H. Keypour, S.Salezadeh, R.D.Pritichand and R.V. Parish, *Inorg Chem.* **11,** 5787,2000

19. M. Kliskic, J. Radosevi, and S. Gudic, *"Pyridine and its derivatives as inhibitors of aluminium corrosion in chloride solution," Journal of Applied Electrochemistry,* vol. 27, no. 6,**947–952**, 1997.
20. M. A. Ameer, E. Khamis, G. Al-senani, *Ads. Sci. Tech.* **18**,177,2000
21. A.Popova,M.Christov,T.Deligeorgiev,*Corrosion* **59,**756,2003.
22. E.E.Oguzie,G.N.Onuoha,A.I.Onuchukwu,Mater.*Chem.Phys*.**89**,305,2004.
23. M.A.Quraishi,H.K.Sharma,*Appl.Electrochem*. **35**,33,2005.
24. P. Deepa Rani and S. Selvaraj, *"Inhibitive and adsorption properties of punica granatum extract on brass in acid media," Journal of Phytology,* vol. 2, no. 11,**58–64**, 2010.
25. M. J. Sanghvi, S. K. Shuklan, A. N. Misra, M. R. Padh, and G. N. Mehta, *"Inhibition of hydrochloric acid corrosion of mild steel by aid extracts of Embilica officianalis, Terminalia bellirica and Terminalia chebula," Bulletin of Electrochemistry,* vol. 13, no. 8-9,**358–361**, 1997.
26. M. J. Shangvi, S. K. Shukla, A. N. Mishra, M. R. padh, and G. N. Mehta, *"Corrosion inhibition of mild steel in hydrochloric acid by acid extracts of Sapindus Trifolianus, Acacia Concian and Trifla,"Transactions of the Metal Finishers Association of India*, vol. 5, no. 3,**143–147**, 1996.
27. N. O. Eddy and E. E. Ebenso, *"Adsorption and inhibitive properties of ethanol extracts of Musa sapientum peels as a green corrosion inhibitor for mild steel in H_2SO_4," African Journal of Pure and Applied Chemistry,* vol. 2, no. 6, **046–054**, 2008.
28. S. Manish Kumar, K. Sudesh, R. Ratnani, and S. P. Mathur, *"Corrosion inhibition of Aluminium by extracts of Prosopis cineraria in acidic media," Bulletin of Electrochemistry,* vol. 22, no. 2,**69–74**, 2006.
29. E. E. Ebenso and U. J. Ekpe, *"Kinetic study of corrosion and corrosion inhibition of mild steel in H_2SO_4 using Parica papaya leaves extract," West African Journal of Biological and Applied Chemistry,* vol. 41,**21–27**, 1996.
30. A. Y. El-Etre, *"Natural honey as corrosion inhibitor for metals and alloys. I. Copper in neutral aqueous solution," Corrosion Science,* vol. 40, no. 11,**1845–1850**, 1998.
31. J. C. Chalchat, R. P. Garry, A. Michet, B. Benjilali, and J. L. Chabart, *"Essential oils of Rosemary (Rosmarinus officinalis L.). The chemical composition of oils of various origins (Morocco, Spain, France)," Journal of Essential Oil Research,* vol. 5, no. 6,**613–618,** 1993.
32. S. A. Umoren and E. E. Ebenso, *"Studies of the anti-corrosive effect of Raphia hookeri exudate gum-halide mixtures for aluminium corrosion in acidic medium," Pigment and Resin Technology,* vol. 37, no. 3,**173–182,** 2008.
33. M. Abdallah, *"Guar gum as corrosion inhibitor for carbon steel in sulphuric acid solutions,"Portugaliae Electrochimica Acta,* vol. 22,**161–175**, 2004.
34. P. C. Okafor, U. J. Ekpe, E. E. Ebenso, E. M. Umoren, and K. E. Leizou, *"Inhibition of mild steel corrosion in acidic medium by Allium sativum extracts," Bulletin of Electrochemistry,* vol. 21, no. 8,**347–352,** 2005.
35. P. C. Okafor and E. E. Ebenso, *"Inhibitive action of Carica papaya extracts on the corrosion of mild steel in acidic media and their adsorption characteristics," Pigment and Resin Technology,* vol. 36, no. 3,**134–140**, 2007.

36. P. C. Okafor, V. I. Osabor, and E. E. Ebenso, *"Eco-friendly corrosion inhibitors: Inhibitive action of ethanol extracts of Garcinia kola for the corrosion of mild steel in H_2SO_4 solutions," Pigment and Resin Technology,* vol. 36, no. 5,**299–305**, 2007.
37. P. C. Okafor, M. E. Ikpi, I. E. Uwah, E. E. Ebenso, U. J. Ekpe, and S. A. Umoren, *"Inhibitory action of Phyllanthus amarus extracts on the corrosion of mild steel in acidic media," Corrosion Science,* vol. 50, no. 8, **2310–2317**, 2008.
38. A. Chetouani, B. Hammouti, and M. Benkaddour, *"Corrosion inhibition of iron in hydrochloric acid solution by jojoba oil," Pigment and Resin Technology,* vol. 33, no. 1,**26–31**, 2004.
39. A. Bouyanzer and B. Hammouti, *"A study of anti-corrosive effects of Artemisia oil on steel," Pigment and Resin Technology,* vol. 33, no. 5,**287–292**, 2004.
40. E. E. Oguzie, *"Studies on the inhibitive effect of Occimum viridis extract on the acid corrosion of mild steel," Materials Chemistry and Physics,* vol. 99,**441–446**, 2006.
41. Pooja Sharma, R. K. Upadhyay,*et. al. JTR Chem* 15(1) **21-27**, 2008.
42. N.Kumpawat, A.Chaturvedi, R. K. Upadhyay. *J Protection pf Metals and Physical of Surfaces.46(2)* ***267-270****,2010*
43. A. Bansiwal, P. Anthony and S.P. Mathur, *Br. Corros.J.* **35**, 301, 2000.
44. R. K. Upadhyay and S.P. Mathur, *J. Electrochem.Soc.Ind.* **2**, 55, 2006.
45. R. K. Upadhyay and S.P. Mathur, *E-Journal of Chem.***3**,4,2007.
46. Anonymous, J. IARC, vol.49,1999.
47. R. K. Upadhyay, S Anthonny and S.P. Mathur, *J. Electrochem.***43**,252,2007.
48. T. Sethi,A.Chaturvedi, R. K. Upadhyay and S.P. Mathur,*J.Chil.Chem.Soc.*, **3**,52,2007
49. T. Sethi,A.Chaturvedi, R. K. Upadhyay and S.P. Mathur,*Polish J. Chem.*, **82**,591,2008.
50. M. Kliskic, J. Radoservic, S. Gudic, and V. Katalinic, *"Aqueous extract of Rosmarinus officinalis L. as inhibitor of Al-Mg alloy corrosion in chloride solution," Journal of Applied Electrochemistry,* vol. 30, no. 7,**823–830**, 2000.
51. A. Y. El-Etre and M. Abdallah, *"Natural honey as corrosion inhibitor for metals and alloys. II. C-steel in high saline water," Corrosion Science,* vol. 42, no. 4,**731–738**, 2000.
52. A. Y. El-Etre, M. Abdallah, and Z. E. El-Tantawy, *"Corrosion inhibition of some metals using lawsonia extract," Corrosion Science,* vol. 47, no. 2,**385–395**, 2005.
53. J.D.Talati and D.K.Gandhi,*Ind.J.Tech*, **29**,277,1997.
54. M.G.Fontana,Corrosion Engineering,3rd edition, Mc Graw Hill Book Company, **173**,1987.
55. K.Aziz and A.M. Shams E1-Din*, Corrosion. Sci*.**,5**,489,1995.
56. F.Mylius,Z.Metalik , **14**,239,1992.
57. Vinod S. Agarwala, *New Methods for Corrosion Testing of Aluminium Alloys*,1134.
58. Joseph Goldstein, Dale E. Newbury, David C. Joy, Charles E. Lyman, Patrick Echlin, Eric Lifshin, Linda Sawyer, J.R. Michael, *Scanning Electron Microscopy and X-ray Microanalysis* (3)